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(54) Lactone-modified epoxy resin
and composition containing such
resin

(57) The present invention relates to a
lactone-modified epoxy resin which is
highly flexible and has improved heat
resistance, water resistance, low-
temperature properties and miscibility.

The present invention also relates to a
method of preparing such a lactone-
modified epoxy resin and to
compositions containing such a resin.

The lactone-modified epoxy resin of
the invention is obtained by reacting
97 to 5 parts by weight of a hydroxyl
group-containing epoxy resin with 3
to 95 parts by weight of ϵ -
caprolactone.

GB 2 101 605 A

SPECIFICATION

Lactone-modified epoxy resin and composition containing such resin

The present invention relates to a lactone-modified epoxy resin and to compositions containing such a resin.

- 5 The present invention also relates to a method of preparing a lactone-modified epoxy resin. 5

An epoxy resin, especially a glycidyl ether type epoxy resin prepared from bisphenol A and epichlorohydrin, includes a great variety of kinds ranging from a liquid resin to a solid resin having a high molecular weight, and this resin is widely used in various fields.

- 10 A liquid resin having a low molecular weight has a high reactivity in the epoxy group, and by utilizing this property, the resin can be cured at normal temperatures with a polyamide or polyamide resin and used as an adhesive, fibre-reinforced plastics (FRP), a flooring material or an anti-corrosive paint. Moreover, the liquid epoxy resin can be heated and cured with a polybasic acid anhydride for the manufacture of cast products especially in the electric industry. 10

- 15 On the other hand, a product having a high molecular weight is a brittle solid resin having a melting point of 60 to 150°C, is widely used as a powdery casting resin in the electric industry by reacting it with an epoxy curing agent such as a polyamide, dicyandiamide, an imidazole or an acid anhydride. Furthermore, since such a resin contains not only terminal epoxy groups but also secondary hydroxyl groups, it is widely used in the field of coating by utilizing the reactivity of these hydroxyl groups. For example, the solid epoxy resin is added to a melamine alkyd type baking paint so as to improve the corrosion resistance and adhesion. Moreover, an epoxy ester obtained by esterification of this solid resin with a fatty acid, e.g. an unsaturated fatty acid, is used as an air-drying or normal temperature-drying paint. Furthermore, this epoxy resin is used as a baking paint including a melamine resin as a cross-linking agent or as a can-coating paint while being combined with a phenolic resin. 15

- 20 Moreover this solid epoxy resin can be powdered and mixed with a blocked isocyanate and can be used as an epoxy type powder paint, or it can be used for cationic electrostatic coating after the epoxy groups have been aminated and rendered water-soluble. Although the solid epoxy resin can be used in various fields, since the resin is hard and brittle and the hydroxyl group is a secondary hydroxyl group, the reactivity with a cross-linking agent to be reacted with the hydroxyl group is poor and a high temperature is required for baking and cross-linking. Moreover, this epoxy resin is defective in that its weatherability is poor or yellowing or chalking is caused. 20

- 25 We have carried out research with a view to eliminating these defects of an epoxy resin and further broadening the possibility of the epoxy resin, and we have found that an appropriate flexibility is given to a hard and brittle epoxy resin by ring-opening polymerization of ϵ -caprolactone with the secondary hydroxyl group of the epoxy resin. In this way the secondary hydroxyl group which is poor from the point of view of reactivity is converted to a primary hydroxyl group of the polycaprolactone having a high reactivity. Also, since the primary hydroxyl group is present in this modified epoxy resin at a point separate from the rigid epoxy resin skeleton, reaction with a cross-linking agent is accelerated. 25

- 30 We have also found that an appropriate flexibility is given to a hard and brittle epoxy resin by ring-opening polymerization of ϵ -caprolactone onto the secondary hydroxyl group if the epoxy resin and further modifying both terminal epoxy groups of the epoxy resin with an amine having an active hydrogen atom. Furthermore, we have found that when the epoxy resin is modified with an amine, the adhesion to a coated article and the corrosion resistance are highly improved. 30

- 35 It is well known to heat-cure an epoxy resin incorporated with a polycarboxylic acid anhydride and with a curing promoter such as an amine, the cured articles have, in general, improved chemical, mechanical, and thermal properties, and find use as electrical parts and other articles in many industrial fields. However, they are very hard, lacking flexibility, and greatly strained by cure shrinkage. Many attempts have been made to overcome the disadvantage of lacking flexibility. For example, it has been attempted to incorporate epoxy resins with metered to render it more flexible such as a polybutadiene oligomer having carboxyl groups at both ends, a polyether resin having hydroxyl groups, a polyester resin, e.g. a polyester resin having carboxyl groups, or a polyamide resin, or with a flexible epoxy resin such as glycidyl ether which is prepared from polyether polyol and epichlorohydrin. The above-mentioned attempts, however, are not necessarily successful because the resulting epoxy resins are poor in heat resistance, chemical resistance, and mechanical strength. In order to develop a curable epoxy resin composition having improved flexibility, we have carried out a series of studies which have shown that this object can be achieved by heat-curing caprolactone-modified epoxy resin and polycarboxylic acid anhydride with a curing promoter. 35

- 40 It is also well known to cure at room temperature, or to heat-cure, an epoxy resin incorporated with a polyamine. The cured articles have, in general, improved chemical, mechanical, and thermal properties, and find use as electrical parts, adhesives, and other particles in many industrial fields. However, they are very hard, lacking flexibility, and greatly strained by cure shrinkage. Many attempts have been made to impart flexibility. For example, it has been attempted to incorporate epoxy resins with material to render it more flexible such as a polybutadiene oligomers having carboxyl groups or hydroxyl groups at both ends, a polyether resin having hydroxy groups, or a polyester resin e.g. a polyester resin having carboxyl groups, or with a flexible epoxy resin like glycidyl ether which is 40

prepared from polyether polyol and epichlorohydrin. The above-mentioned attempts, however, are not necessarily successful because the resulting epoxy resins are poor in heat resistance, chemical resistance, and mechanical strength.

In order to develop a curable epoxy resin composition having improved flexibility, we have carried out a series of studies which have shown that this object can be achieved by curing at room temperature, or heat curing, a caprolactone-modified epoxy resin with a polyamine.

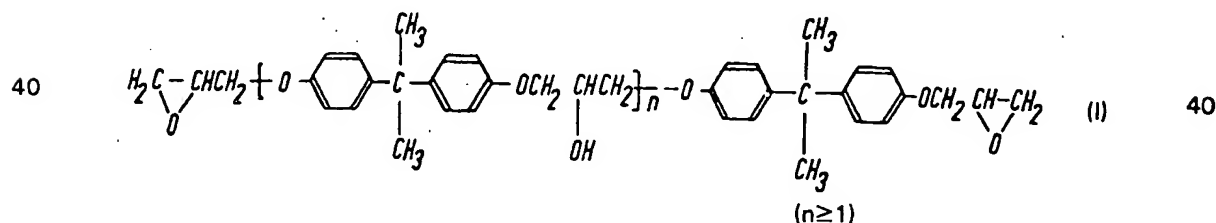
According to the present invention, there is provided a lactone-modified epoxy resin obtained by reacting 97 to 5 parts by weight of a hydroxyl group-containing epoxy resin with 3 to 95 parts by weight of ϵ -caprolactone to effect ring-opening polymerization of ϵ -caprolactone with the hydroxyl group of the epoxy resin.

As means for imparting flexibility to an epoxy resin, a method is known in which the epoxy resin is esterified with a long-chain fatty acid. However, in this modified resin, it is still a secondary hydroxyl group having poor reactivity that reacts with a cross-linking agent, and the number of the hydroxyl groups is reduced as a result of the esterification.

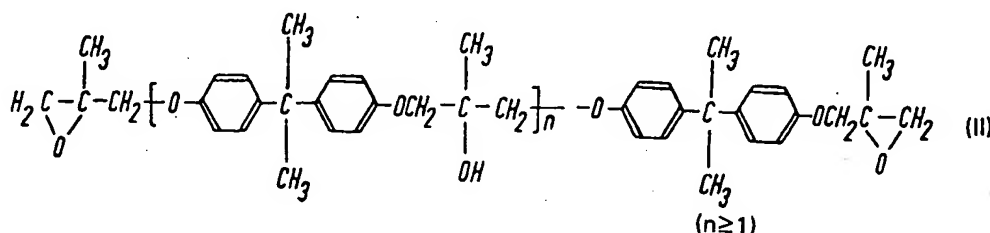
A method is also known in which the epoxy resin is modified with a polyester polyol, polycaprolactone polyol or polyamide resin having flexibility by utilizing the terminal epoxy group of the epoxy resin. This modified resin is used for electrostatic coating. However, in this modified resin, it is still a secondary hydroxyl group having a poor reactivity that is used for the cross-linking reaction. Furthermore, as such secondary hydroxyl groups are directly bonded to the rigid skeleton of the epoxy resin, the reactivity with a cross-linking agent is further reduced. Since the resin of the present invention is distinguished over these known modified epoxy resins in that flexibility is imparted to the epoxy resin of the present invention and, simultaneously, a primary hydroxyl group is given to the epoxy resin, the range of application of the epoxy resin is further broadened and moreover, since the curing reaction with a cross-linking agent is advanced at a temperature lower than that conventionally adopted for the curing reaction, it is possible to achieve a high saving in energy.

The lactone-modified epoxy resin of this invention has polycaprolactone side chains bonded directly to the epoxy resin as the result of the ring opening polymerization of ϵ -caprolactone with hydroxyl groups present in the epoxy resin per se. Therefore, not only is it highly flexible, but it also has improved heat resistance, water resistance, low-temperature properties i.e. improved properties in cold climates, and miscibility which are inherent in polycaprolactone. In the case where epoxy resins are made flexible by adding material rendering them more flexible, the miscibility of the two components often causes a problem. According to the present invention, it is possible to modify any epoxy resins with ϵ -caprolactone so long as the epoxy resins have hydroxyl groups. The present invention is very useful in that it enables one to impart flexibility to curable epoxy resin compositions which are used in every industrial area.

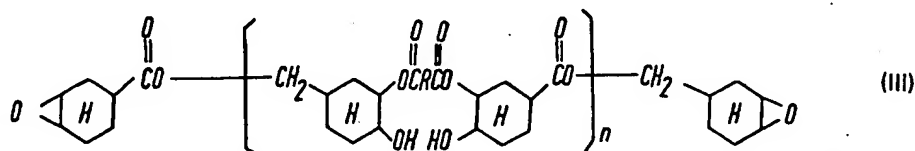
The epoxy resin which is used for producing the lactone-modified epoxy resin according to the present invention can be any epoxy resin so long as it contains a hydroxyl group. Examples of such epoxy resins are bisphenol A diglycidyl ether represented by the following formula (I) which is produced from bisphenol A and epichlorohydrin,



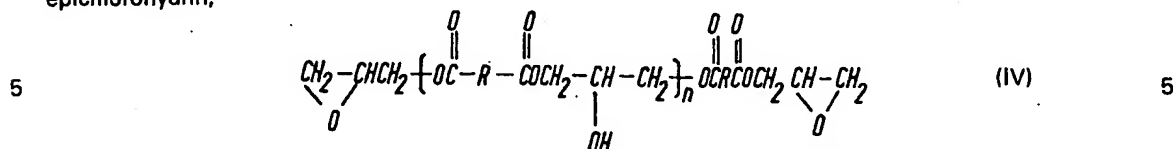
an epoxy resin represented by the following formula (II) which is produced from bisphenol A and B-methylepichlorohydrin,



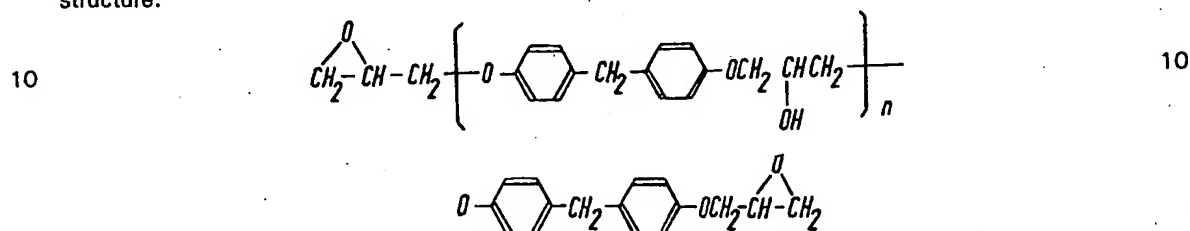
a flame retardant epoxy resin which is produced from 2,6-dibromobisphenol A and epichlorohydrin or β -methylepichlorohydrin, an alicyclic epoxy resin represented by the following formula (III),



($n \geq 1$, R=an alkylene group having 2 to 10 carbon atoms, or a phenylene group) a glycidyl ester represented by the following formula (IV) which is synthesized from dicarboxylic acid and epichlorohydrin,



($n \geq 1$, R=an alkylene group, especially an alkylene group having 2 to 10 carbon atoms, or a divalent aromatic group, especially a phenylene group) and a glycidyl ether epoxy resin which is produced from bisphenol F (synthesized from formalin and phenol) and epichlorohydrin, which has the following structure:



wherein n is a number of at least 1.

The ϵ -caprolactone to be reacted with the epoxy resins having hydroxyl groups is produced industrially by Baeyer-Villiger rearrangement of cyclohexanone with a peracid. As far as the features of the present invention are not damaged it is possible to copolymerize a cyclic lactone together with ϵ -caprolactone.

According to this invention, the epoxy resin and ϵ -caprolactone are reacted at ratios of 97 to 5 parts by weight for the former and 3 to 95 parts by weight for the latter, preferably 95 to 30 parts by weight for the former and 5 to 70 parts by weight for the latter. If the quantity of ϵ -caprolactone for modification is too small, the resulting cured articles are not sufficiently flexible, and if it is too much, the cured articles are excessively flexible.

The reaction of epoxy resin and ϵ -caprolactone may, for example, be performed at 100 to 240°C, preferably 120 to 200°C, in the presence of catalyst. If the reaction temperature is lower than 100°C, the reaction rate is slow, and if it is higher than 240°C, ϵ -caprolactone boils and escapes from the reaction system. A catalyst is required for ϵ -caprolactone to be added to the secondary hydroxyl groups of epoxy resin through the ring opening reaction. Examples of such catalysts are titanium compounds such as for example, tetrabutyl titanate, tetrapropyl titanate, or tetraethyl titanate; organotin compounds such as for example stannous octoate, dibutyltin oxide, or dibutyltin laurate; and stannous halides such as for example, stannous chloride, stannous bromide, or stannous iodide. The stannous halide is preferred when it is desired to obtain a product having a narrow molecular weight distribution. The catalyst may, for example, be used in an amount of 0.01 to 1000 ppm, preferably 0.2 to 500 ppm, depending on the reaction temperature.

The reaction may be performed in the absence of a solvent or in the presence of a solvent, such as for example, toluene or xylene, having no active hydrogen. Any solvent having ester bonds is not preferable, because an ester interchange reaction takes place in the reaction between the ester bond of the polycaprolactone chain and the solvent, forming polycaprolactone which is not connected to the epoxy resin.

When stannous chloride is used as the catalyst, substantially no ester exchange reaction takes place and, hence, an ester type solvent may be used. However, when a titanium type catalyst is used, the ester exchange reaction is promoted, and it is preferred that the use of an ester type solvent be avoided.

Since the lactone-modified epoxy resin so-obtained contains primary hydroxyl groups having a high reactivity, the resin may be used as a cross-linking type coating agent by mixing it with an isocyanate, an amino resin such as for example malimine or a phenolic resin.

Moreover, the modified epoxy resin of the invention may be used as a powder paint by mixing it with a blocked isocyanate. Furthermore, the lactone-modified resin may be added to conventional epoxy resins so as to improve their flexibility or reactivity. Still further, the modified resin may be used for the production of an aqueous resin by reacting the epoxy groups left on both ends of the molecule of the resin with an amine and then neutralising. An aqueous baking paint or electrostatic coating paint

may be prepared by mixing this aqueous resin with a melamine resin as a water-soluble curing agent or with a blocked isocyanate.

Furthermore, an epoxy acrylate resin synthesized by reacting both the terminal epoxy groups of the resin of the present invention with acrylic acid or methacrylic acid may be mixed with a radical initiator or photosensitizer to form a photo-curable or radical-curable resin which is used for fibre-reinforced plastics (FRP), a photo-curable paint, an ink or an adhesive.

Thus, the present invention includes a curable epoxy resin composition which comprises lactone-modified epoxy resin, and polycarboxylic acid anhydride and curing promoter blended therein, said epoxy resin being obtained by ring opening polymerization of 3 to 95 parts by weight of ϵ -caprolactone with 97 to 5 parts by weight of epoxy resin having a hydroxyl group.

Any polycarboxylic acid anhydride can be used for the curable composition of this invention, for example, phthalic anhydride, (methyl)tetrahydrophthalic anhydride, (methyl)hexahydrophthalic anhydride, methyl nadic anhydride, chlorendic anhydride, trimellitic anhydride, pyromellitic anhydride, or dodecanylsuccinic anhydride. They are preferably used in an amount of 0.5 to 1.0 equivalent for one equivalent of epoxy group.

Any curing promoter can be used so long as it has a catalytic action and examples are tertiary amines such as for example benzyldimethylamine, benzyldiethylamine, cyclohexyldimethylamine or tris (dimethylaminomethyl)phenol. They are preferably used in an amount of 0.05 to 5.0 parts by weight for 100 parts by weight of epoxy resin.

The present invention also includes a curable epoxy resin composition which comprises a lactone-modified epoxy resin and a polyamide blended therein, said epoxy resin being obtained by polymerization of 3 to 95 parts by weight of ϵ -caprolactone with 97 to 5 parts by weight of epoxy resin having a hydroxyl group.

Any polyamine can be used for the curable composition of this invention for example aliphatic polyamines such as for example ethylenediamine, diethylenetriamine, triethylenetetramine, menthenediamine, m-xylylenediamine or N-aminoethylpiperazine; aromatic polyamines such as for example *m*-phenylenediamine, diaminodiphenylmethane, or diaminodiphenylsulfone; melamine resin; urea resin; or imidazole amino acid. They are preferably used in an amount of 0.1 to 3.0 equivalent for one equivalent of epoxy group.

In addition, it is also possible to add compounds that promote curing, such as for example, water, alcohols, carboxylic acids, primary amines, or secondary amines having active hydrogen. The composition of this invention may be incorporated with a filler of an inorganic compound such as for example alumina and silica.

Further, the curable epoxy resin composition of this invention may be incorporated with any material for rendering of flexible known to the industry such as for example butane-acrylonitrile copolymer oligomer, polybutadiene dicarboxylic acid, polycaprolactone, dimer acid, or polyether polyol.

The present invention also includes a process for the preparation of coating polyol resins, which comprises partially or totally reacting epoxy groups of a lactone-modified epoxy resin, obtained by reacting 97 to 5 parts by weight of a hydroxyl group-containing epoxy resin with 3 to 95 parts by weight of ϵ -caprolactone to effect ring-open polymerization of the hydroxyl groups of the epoxy resin with ϵ -caprolactone with a primary or secondary amine.

The resin obtained according to the present invention is distinguished over the conventional epoxy resins in that ϵ -caprolactone which is bonded to the hydroxyl group of the epoxy resin by ring-opening polymerization is present as a side chain and imparts flexibility to the epoxy resin and a primary hydroxyl group which has high reactivity is present at the end of the soft side chain separate from the rigid skeleton. Furthermore, in the embodiment of the invention wherein all or part of the epoxy groups are ring-opened by an amine, when the resin is mixed with a curing agent, good stability to storage can be obtained, and because of the presence of nitrogen atoms, the corrosion resistance and adhesion can be improved. Moreover, the hydroxyl group concentration in the resin can optionally be adjusted by using an appropriate amine, for example, an alkanolamine. If these amino groups are neutralized with an acid, the resin can be rendered water-soluble and the neutralized resin can be used as a water-soluble paint or cationic electrostatic coating paint. Still further, if the epoxy resin of the present invention is reacted with an acid anhydride to introduce a carboxyl group in the form of a half ester, the reactivity with a melamine resin is enhanced and a melamine baking paint can be provided. In addition, an anionic water-soluble resin or anionic electrostatic coating paint can be provided by neutralizing the carboxyl group with an amine.

As will be apparent from the foregoing description, according to the present invention, the range of application of an epoxy resin can be broadened in the field of coating and furthermore, since the cross-linking reaction with a melamine resin or isocyanate can be advanced at a temperature lower than the temperature heretofore adopted and the cross-linking density can be increased, a great saving in energy can be attained in the field of coating.

As the primary or secondary amine which may be reacted with all or part of both the terminal groups of the ϵ -caprolactone-modified epoxy resin, there are preferably used amines or alkanolamines represented by the formula H_xNR_y in which H is hydrogen atom N, is a nitrogen atom, R represents an alkyl group having 1 to 12 carbon atoms, a phenyl group, an alicyclic group having 1 to 12 carbon

atoms or a hydroxyl group-containing alkyl group having 1 to 12 carbon atoms, x is 1 or 2, and y is 1 or 2. For example, there can be mentioned dimethylamine, diethylamine, methylethylamine, dipropylamine, propylethylamine, butylethylamine, dibutylamine, dipentylamine, dihexylamine, ethylcyclohexylamine, dioctylamine, didodecylamine, diethanolamine, di-n-propanolamine.

- 5 diisopropanolamine or di-2-hydroxydodecylamine. Furthermore, there may be used amines substituted with an aromatic group such as for example, benzylmethylamine, benzylethylamine, benzylethanolamine, benzylpropanolamine or dibenzylamine. The reaction between the ϵ -caprolactone-modified epoxy resin and the amine may, for example, be carried out at 80 to 200°C, preferably 100 to 180°C. 5

- 10 The reaction may be carried out in the absence of a solvent or in the presence of a solvent having no active hydrogen, such as toluene or xylene. 10

- Since the resin of the present invention contains a hydroxyl group, a carboxyl group can be introduced into the resin by reacting it with a polybasic acid or polybasic acid anhydride. As the acid anhydride there may be used for example maleic anhydride, succinic anhydride, phthalic anhydride, 15 trimellitic anhydride or hexahydrophthalic anhydride. When the resin of the present invention is mixed with a melamine resin and used as a baking paint, it is preferred that the carboxyl group be introduced so that the acid value is 2 to 50 KOH mg/g, especially 5 to 30 KOH mg/g. A resin having an acid value of 20 to 50 KOH mg/g may be used as an anionic type water-soluble resin paint in various fields after it has been neutralized with a basic substance such as for example an amine or caustic soda. Moreover, if 20 the nitrogen atom contained in the resin of the present invention is neutralized with an organic acid, the resin can be converted to a cationic water-soluble resin and used for a cationic electrostatic coating paint. 20

- Since the resin of the present invention has a primary hydroxyl group having a high activity, the resin of the present invention can be used as a baking paint by combining it with a melamine resin or 25 amino resin or as a room temperature-drying or baking curing paint by combining it with an isocyanate or blocked isocyanate. 25

Moreover, the resin of the present invention may be used for the modification of coating compositions by incorporating it into a polyester resin, an acrylic resin, a cellulose resin such as for example nitrocellulose acetate butyrate, a vinyl chloride resin, a petroleum resin or an alkyd resin.

- 30 The invention will now be further illustrated by way of the following examples:—
Examples 1 to 9 concern the ϵ -caprolactone-modified epoxy resin. Application Examples 1 to 8 concern coating of the modified epoxy resin. Composition Examples 1 and 2 concern the composition comprising the modified epoxy resin, a carboxylic anhydride and a promoter for curing. Composition Examples 3 and 4 concern the modified epoxy resin and a polyamine. Examples 10 to 13 concern the 35 modified epoxy resin which has been further reacted with an amine. Application Examples concern coating of the modified epoxy resin which has been further reacted with an amine. 35

All references to part are based on weight throughout the Examples and the comparative Examples.

Example 1

- 40 A four-neck flask equipped with a nitrogen-introducing tube, a thermometer, a condenser and a stirrer was charged with 1000 parts of Araldite 6097 (an epoxy resin available from Ciba-Geigy Co.) having a melting point of 130°C, 111 parts of ϵ -caprolactone and 0.011 part of tetrabutyl titanate, and reaction was carried out at 180°C for 5 hours to obtain a solid resin having a melting point of 81 to 85°C, a hydroxyl value of 179 KOH mg/g and an epoxy equivalent of 3070. 40

45 Examples 2 to 5

In the same reaction vessel as used in Example 1 various epoxy resins were reacted at various ratios with ϵ -caprolactone to obtain lactone-modified epoxy resins. The results obtained are shown in Table 1. The araldite resins are available from Ciba-Geigy. 45

Table 1

Composition		Example 2	Example 3	Example 4	Example 5	
<i>Epoxy resin</i>						
5	Araldite 6097 (m.p.=130°C)	1000				5
	Araldite 6084 (m.p.=100°C)		1000			
	Araldite 6071 (m.p.=70°C)			2250	2000	
	ε-caprolactone	250	111	250	500	
	tetrabutyl titanate	0.0125	0.011	0.025	0.025	
<i>Reaction conditions</i>						
10	reaction temperature (°C)	180	180	170	170	10
	reaction time (hours)	4	4	5	6	
<i>Properties</i>						
	melting point (°C)	61—65	67—73	33—36	below 30	
15	hydroxyl value (KOH mg/g)	166	192	215	190	15
	epoxy equivalent	3910	1630	544	608	
Example 6						
20	Into a four-necked flask equipped with a nitrogen introducing tube, a thermometer, a condenser, and a stirrer were charged 2000 parts of epoxy resin (Araldite GY-250, available from Ciba-Geigy, epoxy equivalent 185 produced from bisphenol A and epichlorohydrin, 200 parts of ε-caprolactone, and 0.022 part of tetrabutyl titanate. Reaction was carried out under a nitrogen stream at 170°C for 8 hours.					20
25	The quantity of unreacted ε-caprolactone was 0.62%. The resulting resin was a viscous liquid having an epoxy equivalent of 207, a viscosity (Gardner) of Z ₄ , an acid value of 0.06, and a Gardner colour scale lower than 1.					25
Example 7						
30	Into the same apparatus as used in Example 6 were charged 1800 parts of Araldite GY-250, 360 parts of ε-caprolactone, and 0.022 part of tetrabutyl titanate. Reaction was carried out under a nitrogen stream at 170°C for 8 hours.					30
	The quantity of unreacted ε-caprolactone was 0.48%. The resulting resin was a viscous liquid having an epoxy equivalent of 255, a viscosity (Gardner) of Z ₄ , an acid value of 0.05, and a Gardner colour scale lower than 1.					
Example 8						
35	Into a four-necked flask equipped with a nitrogen introducing tube, a thermometer, a condenser, and a stirrer were charged 2000 parts of epoxy resin (Araldite GY-250, available from Ciba-Geigy, epoxy equivalent 185) produced from bisphenol A and epichlorohydrin, 200 parts of ε-caprolactone, and 0.022 part of tetrabutyl titanate. Reaction was carried out under a nitrogen stream at 170°C for 8 hours.					35
40	The quantity of unreacted ε-caprolactone was 0.62%. The resulting resin was a viscous liquid having an epoxy equivalent of 210, a viscosity (Gardner) of Z ₆ , an acid value of 0.03, and a Gardner colour scale lower than 1.					40
Example 9						
45	Into the same apparatus as used in Example 8 were charged 1800 parts of Araldite GY-250, 360 parts of ε-caprolactone, and 0.022 part of tetrabutyl titanate. Reaction was carried out under a nitrogen stream at 170°C for 8 hours.					45
	The quantity of unreacted ε-caprolactone was 0.31%. The resulting resin was a viscous liquid having an epoxy equivalent of 230, a viscosity (Gardner) of Z ₄ , an acid value of 0.05, and a Gardner colour scale lower than 1.					
Application Examples 1 to 8 and Comparative Examples 1 and 2						
50	The lactone-modified epoxy resins and the unmodified epoxy resin were independently dissolved in ethyl monoglycol acetate, and cross-linking agents were added to the solutions so that the epoxy resin/crosslinking agent weight ratio was 90/10. Then, the coating compositions were independently coated on polished soft steel plates having a thickness of 0.3 mm, and were then dried and cured.					50
55	The following cross-linking agents were used.					
	(1) HMDI (hexamethylene diisocyanate) adduct (Duranate 24A100 supplied by Asahi Kasei Kogyo K. K.)					55
	(2) XDI (xylene diisocyanate) adduct (Takenate D-110N supplied by Takeda Yakuhin Kogyo K. K.)					

(3) IPDI (isophotone diisocyanate) trimer (IPDIT-1890 supplied by Huls Chemical Co.)

(4) Isobutylated melamine (Uban 62 supplied by Mitsui Toatsu Kagaku K. K.)

The results obtained are shown in Table 2.

Table 2

<i>Composition</i>	<i>Application Example 1</i>	<i>Application Example 2</i>	<i>Application Example 3</i>	<i>Application Example 4</i>	<i>Application Example 5</i>
epoxy resin	Example 1	Example 2	Example 3	Example 4	Example 5
cross-linking agent	HMDI adduct	HMDI adduct	HMDI adduct	HMDI adduct	HMDI adduct
<i>Curing conditions</i>					
temperature (°C)	80	80	80	80	80
time (minutes)	120	120	120	120	120
<i>Properties of coatings</i>					
pencil hardness (Mitsubishi Uni)	HB	H	HB	B	B
square cut adhesion	100/100	100/100	100/100	100/100	100/100
impact resistance 500 g (cm)	50	50	30	20	50
Eirchsen value (mm)	8	above 9	above 9	above 9	above 9
bending resistance (2 mm)	○	○	x	○	○
alkali resistance (25°C, 5% NaOH, 48 hours)	○	○	○	○	○
acid resistance (25°C, 5% HCl, 48 hours)	○	○	○	○	○
water resistance (50°C, 48 hours)					
whitening	not	not	observed	observed	not
blister	not	not	not	observed	not
square cut adhesive	100/100	30/100	100/100	100/100	100/100
cellophane tape					
solvent resistance (xylene)	○	○	△	○	○

Table 2 (continued)

<i>Composition</i>	<i>Comparative Example 1</i>	<i>Application Example 6</i>	<i>Application Example 7</i>	<i>Application Example 8</i>	<i>Comparative Example 2</i>
epoxy resin	Araldite 6084	Example 2	Example 2	Example 2	Araldite 6084
cross-linking agent	HMDI adduct	XDI adduct	IPDI trimer	isobutylated melamine	isobutylated melamine
<i>Curing conditions</i>					
temperature (°C)	80	80	80	150	150
time (minutes)	120	120	120	20	20
<i>Properties of coatings</i>					
pencil hardness (Mitsubishi Uni)	H	H	2H	HB	H
square cut adhesion	0/100	100/100	100/100	100/100	90/100
impact resistance 500 g (cm)	10	50	50	50	10
Eirchsen value (mm)	3	above 9	above 9	8	3
bending resistance (2 mm)	x	○	○	○	x
alkali resistance (25°C, 5% NaOH, 48 hours)	○	○	○	○	○
acid resistance (25°C, 5% HCl, 48 hours)	○	○	○	○	○
water resistance (50°C, 48 hours)					
whitening	observed	observed	not	observed	observed
blister	observed	observed	not	not	not
square cut adhesive	100/100	0/100	0/100	100/100	0/100
cellophane tape					
solvent resistance (xylene)	x	○	○	○	x

From the results of Comparative Examples 1 and 2, it is seen that only brittle coatings having no flexibility can be obtained from an epoxy resin not modified with ϵ -caprolactone. From the results of Application Examples 1 to 8, it will be understood that cured coatings excellent from the point of view of flexibility, adhesion and solvent resistance can be obtained from ϵ -caprolactone-modified epoxy resins of the present invention.

In Table 2 the mark "O" indicates good; "Δ" indicates normal; and "x" indicates bad.

Composition Example 1

Fifty parts of the lactone-modified epoxy resin prepared in Example 6 were blended with 36.5 parts of methyltetrahydrophthalic anhydride ("Rikasil MH-700, made by Shin-Nippon Rika Co., Ltd.) and 0.43 part of benzyldimethylamine as a catalyst. After pre-curing at 100°C for 2 hours, the compound was cured at 160°C for 5 hours. Table 3 shows the heat distortion temperature, elongation at break, and breaking strength of the cured resin.

Composition Example 2

Fifty parts of the lactone-modified epoxy resin prepared in Example 7 were blended with 33.6 parts of methyltetrahydrophthalic anhydride and 0.42 part of benzyldimethylamine as a catalyst. The compound was cured under the same conditions as in Composition Example 1. The properties of the cured resin as shown in Table 3.

Comparative Example 3

A composition was prepared by blending 50 parts of unmodified epoxy resin Araldite GY-250 with 40.9 parts of methyltetrahydrophthalic anhydride and 0.45 part of benzyldimethyl amine. The composition was cured under the same conditions as in Composition Example 1. The properties of the cured resin are shown in Table 3.

Comparative Example 4

A composition was prepared by blending 50 parts of unmodified epoxy resin Araldite GY-250 with 40.9 parts of methyltetrahydrophthalic anhydride, 12.5 parts of polycaprolactone triol ("Plascel 308" made by Daicel Chemical Industry Co., Ltd.) as a catalyst, and 0.52 part of benzyldimethyl amine. The composition was cured under the same conditions as in Composition Example 1. The properties of the cured resin are shown in Table 3. As shown in Composition Examples 1 and 2 and Comparative Examples 3 and 4, the curable composition of lactone-modified epoxy resin of this invention not only has outstanding flexibility but also a heat distortion temperature which is higher than that of a composition prepared by simply adding a material promoting flexibility.

Table 3

	Formulation (parts by weight)	Composition Example 1	Composition Example 2	Comparative Example 3	Comparative Example 4
35	Epoxy resin	Example 6 50	Example 7 50	Araldite GY-250 50	Araldite GY-250 50
40	Acid anhydride	Rikasil MH-700 36.5	Rikasil MH-700 33.6	Rikasil MH-700 40.9	Rikasil MH-700 40.9
	Flexibilizer	—	—	—	Placel 308 12.5
45	Catalyst	Benzyldi- methylamine 0.43	Benzyldi- methylamine 0.42	Benzyldi- methylamine 0.45	Benzyldi- methylamine 0.52
	<i>Properties of cured resin</i>				
	Heat distortion temperature (°C)	113	93	131	88
50	Breaking strength (kg/cm ²)	7.52	7.10	8.09	6.82
	Elongation at break (%)	6.62	6.45	6.86	5.83

Composition Example 3

One hundred parts of the lactone-modified epoxy resin prepared in Example 8 were blended with 25.8 parts of diaminodiphenylmethane (abbreviated as DDM hereinafter). After pre-curing at 130°C for 2 hours, the compound was cured at 150°C for 4 hours. Table 4 shows the heat distortion temperature, impact strength, elongation at break, and breaking strength of the cured resin. 5

Composition Example 4

One hundred parts of the lactone-modified epoxy resin prepared in Example 9 were blended with 22.8 parts of DDM, and the compound was cured under the same conditions as in Composition Example 3. The properties of the cured resin are shown in Table 4.

Comparative Example 5

A composition was prepared by blending 100 parts of unmodified epoxy resin Araldite GY-250 with 28.3 parts of DDM, and was cured under the same conditions as in Composition Example 3. The properties of the cured resin are shown in Table 4. 10

Comparative Example 6

A composition was prepared by blending 100 parts of unmodified epoxy resin Araldite GY-250 with 28.3 parts of DDM, and 10 parts of polycaprolactone triol ("Placsel 308" made by Daicel Chemical Industry Co., Ltd.) as a material promoting flexibility. The composition was cured under the same conditions as in Composition Example 3. The properties of the cured resin are shown in Table 4. 15

Comparative Example 7

A composition was prepared by blending 100 parts of unmodified epoxy resin Araldite GY-250 with 28.3 parts of DDM, and 20 parts of "Placsel 308" as a material promoting flexibility. The composition was cured under the same conditions as in Composition Example 3. The properties of the cured resin are shown in Table 4. As shown in Composition Examples 3 and 4 and Comparative Examples 5, 6 and 7, the curable composition of lactone-modified epoxy resin of this invention only not has outstanding flexibility but also a heat distortion temperature which is higher than that of a composition prepared by simply adding a material promoting flexibility. 20 25

Table 4

<i>Formulation (parts by weight)</i>		<i>Composition Example 3</i>	<i>Composition Example 4</i>	<i>Comparative Example 5</i>	<i>Comparative Example 6</i>	<i>Comparative Example 7</i>	
30	Resin of Example 6	100					30
	Resin of Example 7		100				
	Araldite GY-250			100	100	100	
	Placsel 308				10	20	
	DDM	25.8	22.8	28.3	28.3	28.3	
35	<i>Properties of cured resin</i>						35
	Heat distortion temperature (°C)	122	90	166	124	97	
	Tensile strength (kgf/mm ²)	7.3	7.6	7.0	6.4	7.0	
	Tensile elongation (%)	4.8	3.9	5.7	3.0	3.6	
40	Impact strength (Izod with notch) (kgf · cm/cm ²)	4.0	3.5	3.8	3.9	3.3	40

Example 10

A four-neck flask equipped with a thermometer, a nitrogen-introducing tube, a stirrer and a cooler was charged with 720 parts of Epitote YD-011 (bisphenol type epoxy resin supplied by Toto Kasei K. K. and having an epoxy equivalent of 450 to 500), 547 parts of ϵ -caprolactone and 0.013 part of tetrabutyl titanate as the catalyst, and reaction was carried out in a nitrogen current at 170°C for 8 hours. When the amount of residual ϵ -caprolactone was 0.3%, the reaction mixture was cooled to 140°C. Then, 168 parts of diethanolamine were added and reaction was carried out at 140 to 150°C for 1 hour. Then, 38 parts of phthalic anhydride were added to the reaction mixture and the mixture was heated at 150°C for 1 hour to complete the reaction. The reaction mixture was diluted with xylene. The resin solution obtained had a non-volatile component content of 70.2%, a Gardner viscosity of Z₅, a hue of 2, an acid value of 5.6 and a hydroxyl value of 168. 45 50

Example 11

The same reaction vessel as used in Example 10 was charged with 800 parts of Araldite 6084 (a bisphenol type epoxy resin supplied by Ciba-Geigy Co. and having an epoxy equivalent of 900 to 1000), 200 parts of ϵ -caprolactone and 0.01 part of tetrabutyl titanate as the catalyst, and the reaction 55

was carried out at 175°C for 5 hours. The reaction mixture was cooled to 140°C and 91.3 parts of diethanolamine were added, and the reaction was carried out at 140°C for 1 hour. Then, 14.4 parts of phthalic anhydride were added to the reaction mixture, and the mixture was heated at 140°C for 1 hour to complete the reaction. The reaction product was dissolved in a 50/50 mixed solvent of xylene and ethylene glycol monoethyl ether acetate to obtain a resin solution having a non-volatile component content of 51.2%, an acid value of 2.01, a hydroxyl value of 129.2 and a Gardner viscosity of ST (25°C).

Example 12

The same reaction vessel as used in Example 10 was charged with 720 parts of Araldite 6071 (a bisphenol type epoxy resin supplied by Ciba-Geigy Co. and having an epoxy equivalent of 450 to 500), 342 parts of ϵ -caprolactone and 0.01 part of tetrabutyl titanate as the catalyst, and the reaction was carried out at 170°C for 4 hours. The reaction mixture was cooled to 140°C and 168 parts of diethanolamine were added, and the reaction was carried out at 140°C for 1 hour. The reaction product was dissolved in a 50/50 mixed solvent of xylene and ethylene glycol monoethyl ether acetate to obtain a resin solution having a non-volatile component content of 60.1%, an acid value of 1.2 a hydroxyl value of 177, a Gardner viscosity of Z₃ (25°C) and a hue of 1.

Example 13

The same reaction vessel as used in Example 10 was charged with 700 parts of Araldite 6084, 300 parts of ϵ -caprolactone and 0.01 part of tetrabutyl titanate, and the reaction was carried out at 170°C for 6 hours. The reaction mixture was cooled to 140°C and 80 parts of diethanolamine were added, and the reaction was carried out at 140°C for 1 hour to complete the reaction. The reaction product was dissolved in a 50/50 mixed solvent of xylene and ethylene glycol ether acetate to obtain a resin solution having a non-volatile component content of 50.5%, an acid value of 0.3, a hydroxyl value of 115 and a Gardner viscosity of P—Q.

25 Application Examples 9 to 12 and Comparative Examples 8, 9

Coating compositions prepared by mixing the resins of the present invention obtained in Examples 10 to 13 respectively or conventional epoxy resin with curing agents were independently coated on polished soft steel plates having a thickness of 0.3 mm and the coated compositions were dried and cured to obtain cured coatings having a thickness of about 50 to about 70 μ .

30 The following curing agents were used.

(1) HMDI (hexamethylene diisocyanate) adduct (Duranate 24A-100 supplied by Asahi Kasei Kogyo K. K.)

(2) n-Butylated melamine (Uban 20SE supplied by Mitsui Toatsu Kagaku K. K.).

35 The properties of the coatings are shown in Table 5, in which the mark "⊙" indicates excellent; "O" indicates good; "Δ" indicates normal; and "x" indicates bad.

Table 5
Properties of coatings

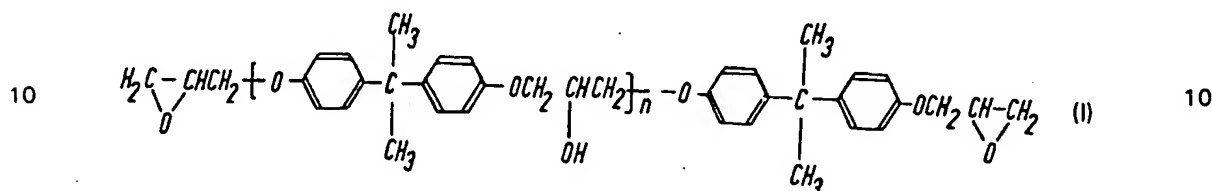
	Application Example 9	Application Example 10	Application Example 11	Application Example 12	Comparative Example 8	Comparative Example 9
resin	Example 10	Example 11	Example 12	Example 13	Araldite 6084	Araldite 6084
Curing agent	Urban 20SE	Duranate	Duranate	Duranate	Duranate	Urban 20SE
resin/curing agent ratio	70/30 (weight ratio)	24A-100 1/0.3 (OH/NCO)	24A-100 1/0.3 (OH/NCO)	24A-100 1/0.3 (OH/NCO)	24A-100 1/0.3 (OH/NCO)	70/30 (weight ratio)
temperature (°C)	120	25	25	25	25	120
time	30 (minutes)	7 (days)	7 (days)	7 (days)	7 (days)	7 (days)
Properties of coatings	<p>pencil hardness (Mitsubishi Uni)</p> <p>square cut adhesion</p> <p>impact resistance 500 g (cm)</p> <p>Erichsen value (mm)</p> <p>bending resistance (2 mm)</p> <p>water resistance (40°C, 100 hours)</p> <p>salt spray resistance (35°C, 150 hours)</p> <p>stain resistance</p> <p>solvent resistance</p> <p>alkali resistance</p>	<p>HB</p> <p>100/100</p> <p>50<</p> <p>8.9</p> <p>good</p> <p>○</p> <p>⊙</p> <p>○</p> <p>⊙</p> <p>⊙</p>	<p>H</p> <p>100/100</p> <p>50<</p> <p>9.0</p> <p>good</p> <p>○</p> <p>⊙</p> <p>Δ</p> <p>⊙</p> <p>⊙</p> <p>⊙</p>	<p>HB</p> <p>100/100</p> <p>50<</p> <p>9.0</p> <p>good</p> <p>○</p> <p>⊙</p> <p>Δ</p> <p>○</p> <p>⊙</p>	<p>H</p> <p>0/100</p> <p>10</p> <p>3</p> <p>bad</p> <p>x</p> <p>Δ</p> <p>⊙</p> <p>x</p> <p>⊙</p>	<p>H</p> <p>90/100</p> <p>10</p> <p>3</p> <p>bad</p> <p>x</p> <p>Δ</p> <p>⊙</p> <p>Δ</p> <p>⊙</p>

Claims

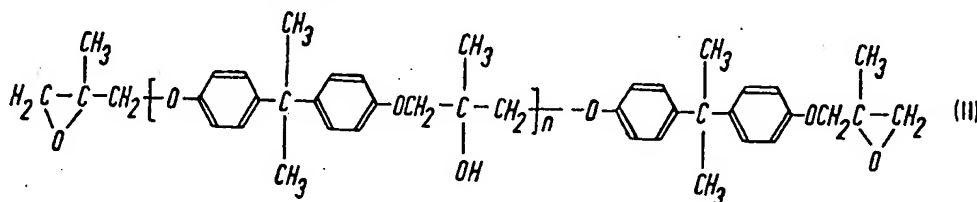
1. A lactone-modified epoxy resin obtained by reacting 97 to 5 parts by weight of a hydroxyl group-containing epoxy resin with 3 to 95 parts by weight of ϵ -caprolactone.

2. A lactone-modified epoxy resin as claimed in claim 1, which is obtained by reacting 95 to 30 parts by weight of the hydroxyl group-containing epoxy resin with 5 to 70 parts by weight of the ϵ -caprolactone.

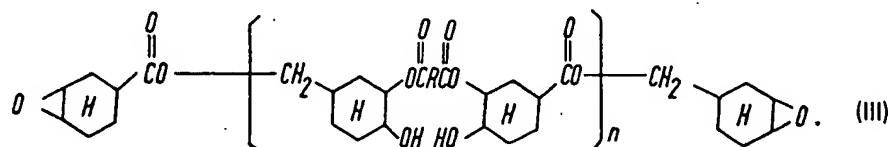
3. A lactone-modified epoxy resin as claimed in claim 1 or claim 2, in which the hydroxyl group-containing epoxy resin is a bisphenol A diglycidyl ether represented by the following formula (I) which is produced from bisphenol A and epichlorohydrin,



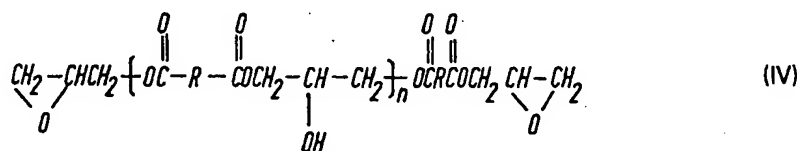
wherein n is at least 1, an epoxy resin represented by the following formula (II) which is produced from bisphenol A and β -methylepichlorohydrin,



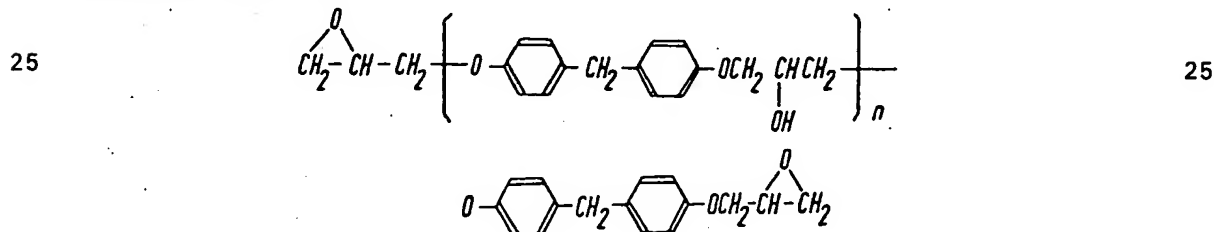
wherein n is at least 1, a flame retardant epoxy resin which is produced from 2, 6-dibromobisphenol A and epichlorohydrin or β -methylepichlorohydrin, an alicyclic epoxy resin represented by the following formula (III),



wherein n is at least 1, and R is an alkylene group having 2 to 10 carbon atoms or a phenylene group, a glycidyl ester represented by the following formula (IV) which is synthesized from dicarboxylic acid and epichlorohydrin,



wherein n is at least 1, and R is an alkylene group or an aromatic group, or a glycidyl ether epoxy resin which is produced from bisphenol F (synthesized from formalin and phenol) and epichlorohydrin, which has the following structure:



wherein n is a number of at least 1.

4. A lactone-modified epoxy resin as claimed in any of claims 1 to 3, in which all or part of the epoxy groups have been reacted with a primary or secondary amine.

5. A lactone-modified epoxy resin as claimed in claim 4, in which the primary or secondary amine is represented by the formula H_xNR_y wherein R represents an alkyl group having 1 to 12 carbon atoms, a phenyl group, an alicyclic group having 1 to 12 carbon atoms, or a hydroxyl group-containing alkyl group having 1 to 12 carbon atoms, x is 1 or 2, and y is 1 or 2.

6. A curable epoxy resin composition which comprises a lactone-modified epoxy resin as claimed in any of claims 1 to 5 a polycarboxylic acid anhydride and a promoter for curing.

7. A curable epoxy resin composition as claimed in claim 6, in which the polycarboxylic acid anhydride is present in an amount of 0.5 to 1.0 equivalent for one equivalent of epoxy group.

5 8. A curable epoxy resin composition as claimed in claim 6 or claim 7, in which the polycarboxylic acid anhydride is phthalic anhydride, (methyl) tetrahydrophthalic anhydride, (methyl) hexahydrophthalic anhydride, methyl nadic anhydride, chlorendic anhydride, trimellitic anhydride, pyromellitic anhydride or dodecenylsuccinic anhydride.

9. A curable epoxy resin composition as claimed in any of claims 6 to 8, in which the promoter is used in an amount of 0.05 to 5.0 parts by weight for 100 parts by weight of epoxy resin.

10 10. A curable epoxy resin composition as claimed in any of claims 6 to 9, in which the promoter is benzyldimethylamine, benzyldiethylamine, cyclohexyldimethylamine or tris (dimethylaminomethyl) phenol.

11. A curable epoxy resin composition which comprises a lactone-modified epoxy resin as claimed in any of claims 1 to 5 and a polyamine.

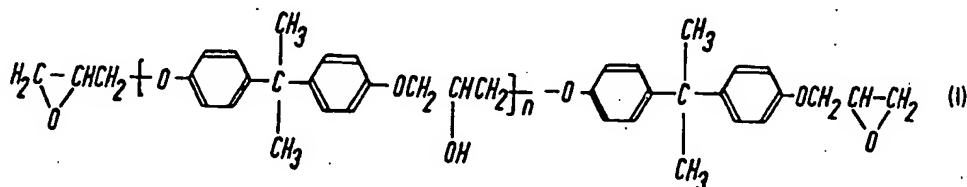
12. A curable epoxy resin composition as claimed in claim 11, in which the polyamine is used in an amount of 0.1 to 3.0 equivalent for one equivalent of epoxy group.

13. A curable epoxy resin composition as claimed in claim 11 or claim 12, in which the polyamide is an aliphatic polyamine, an aromatic polyamine, a melamine resin, a urea resin, or an imidazole amino acid.

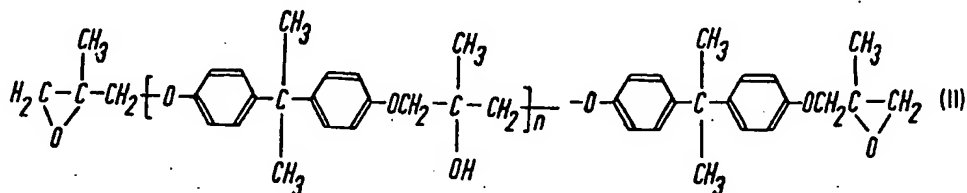
14. A method of preparing a lactone-modified epoxy resin, which comprises reacting 97 to 5 parts by weight of a hydroxyl group-containing epoxy resin with 3 to 95 parts by weight of ϵ -caprolactone.

15. A method as claimed in claim 14, in which 95 to 30 parts by weight of the hydroxyl group-containing epoxy resin are reacted with 5 to 70 parts by weight of the ϵ -caprolactone.

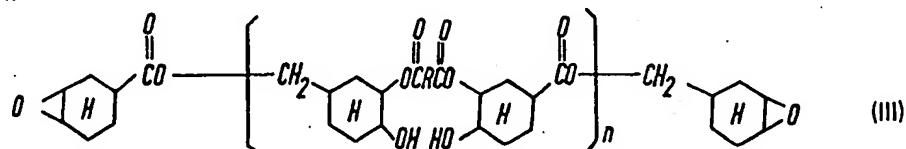
16. A method as claimed in claim 14 or claim 15, in which the hydroxyl group-containing epoxy resin is a bisphenol A diglycidyl ether represented by the following formula (I) which is produced from bisphenol A and epichlorohydrin,



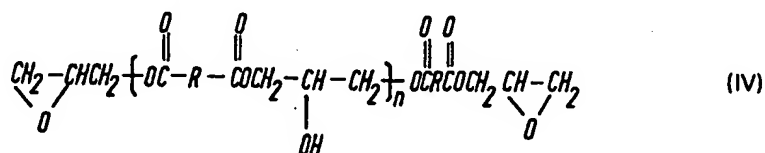
30 wherein n is at least 1, an epoxy resin represented by the following formula (II) which is produced from bisphenol A and β -methylpichlorohydrin,



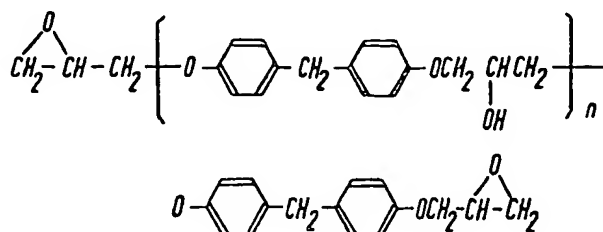
wherein n is at least 1, a flame retardant resin which is produced from 2, 6-dibromobisphenol A and epichlorohydrin or β -methylpichlorohydrin, an alicyclic epoxy resin represented by the following formula (III),



wherein n is at least 1 and R is an alkylene group having 2 to 10 carbon atoms or a phenylene group, a glycidyl ester represented by the following formula (IV) which is synthesized from dicarboxylic acid and epichlorohydrin,



wherein n is at least 1, and R is an alkylene group or an aromatic group, or a glycidyl ether epoxy resin which is produced from bisphenol F (synthesized from formalin and phenol) and epichlorohydrin, which has the following structure:



5

5

wherein n is a number of at least 1.

17. A method as claimed in any of claims 14 to 16, which is performed at a temperature of 100 to 240°C.

18. A method as claimed in claim 17 which is performed at a temperature of 120 to 200°C.

10 19. A method as claimed in any of claims 14 to 18, in which the reaction between the hydroxyl group-containing epoxy resin and the ϵ -caprolactone is carried out in the presence of a catalyst. 10

20. A method as claimed in claim 19, in which the catalyst is used in an amount of 0.01 to 1000 ppm.

15 21. A method as claimed in claim 20, in which the catalyst is used in an amount of 0.2 to 500 ppm. 15

22. A method as claimed in any of claims 19 to 21, in which the catalyst is tetrabutyl titanate, tetrapropyl titanate, tetraethyl titanate, stannous octoate, dibutyltin oxide, dibutyltin laurate, stannous chloride, stannous bromide or stannous iodide.

20 23. A method as claimed in any of claims 14 to 22, in which the reaction between the hydroxyl group-containing epoxy resin and the ϵ -caprolactone is performed in the presence of a solvent having no active hydrogen. 20

24. A method as claimed in claim 23, in which the solvent is toluene or xylene.

25. A method as claimed in any of claims 14 to 24, in which all or part of the epoxy groups of the lactone-modified epoxy resin are reacted with a primary or secondary amine.

25 26. A method as claimed in claim 25, in which the primary or secondary amine is represented by the formula H_xNR_y , wherein R represents an alkyl group, an aromatic group, an alicyclic group or a hydroxyl group-containing alkyl group, x is 1 or 2, and y is 1 or 2. 25

27. A method as claimed in claim 25 or claim 26, in which the reaction between the lactone-modified epoxy resin and the amine is carried out at 80 to 200°C.

30 28. A method as claimed in claim 27, in which the reaction between the lactone-modified epoxy resin and the amine is carried out at 100 to 180°C. 30

29. A lactone-modified epoxy resin as claimed in claim 1 and substantially as hereinbefore described with reference to the Examples.

30. A method of preparing a lactone-modified epoxy resin as claimed in claim 14 and substantially as hereinbefore described with reference to the Examples. 35